XIV. Note on capillarity constants of crystal faces

Harold Hilton

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of sodium could be shown in the same way, though the one experiment that I tried with it gave negative results.

I expect in the near future to investigate all of the questions which I have touched upon in the latter part of this paper, for it appears to me that, with proper coaxing, sodium vapour may furnish us with much information regarding molecular dynamics. The results obtained up to the present time are only a small beginning, but appear to indicate that in sodium vapour we have a medium which approaches more nearly to the ideal absorbing medium, with but a single natural period of vibration, than any substance heretofore investigated.

Of course I am speaking here only with reference to the natural vibration which appears to influence the dispersion. Strictly speaking there are two natural periods of course, which influence the velocity of the light in the medium, but when the medium is very dense the condition certainly approaches very nearly to that of a single period medium. As I have said before, the fluted absorption-bands are without influence on the dispersion, at least their influence is too slight to be detected by the methods that have been employed thus far.

XIV. *Note on Capillarity Constants of Crystal Faces.*

By HAROLD HILTON*.

ON page 520 of the 34th volume of the *Zeitschr. f. Kryst. u. Min.* G. Wulff gives a very interesting theorem; he says:—"Nehmen wir an, dass wir ein Polyöder mit gegebenen Flächenrichtungen, welche durch die Normalen $n_1, n_2, n_3, \dots$ bestimmt werden, gefunden haben, welches der Bedingung des Minimums der Oberflächenenergie bei gegebenem Volumen Genüge leistet. Es ist einleuchtend, dass alle Polyöder welche dem letzteren ähnlich sind und nur durch ihre Volumen sich von einander unterscheiden, ebenfalls dieser Bedingung Genüge leisten werden. Alle dieser Polyöder werden einen Krystall in verschiedenen Wachstumsstadien vorstellen, wobei es klar ist, dass der Wachstumsanfang mit dem letzten Centrum der Aehnlichkeit der ganzen erhaltenen Polyöderreihe zusammenfallen muss. Auf solche Weise kann man die Oberfläche eines dieser Polyöder folgendermassen ausdrücken: $p(n_1^2 + n_2^2 + n_3^2 + \dots)$, wo p eine Constant ist, und die Oberflächenenergie E bei den Capillaritätsconstanten $k_1, k_2, k_3, \dots$ auf den verschiedenem Flächen

$$E = p(k_1 n_1^2 + k_2 n_2^2 + k_3 n_3^2 + \dots)$$

* Communicated by the Author.

sein wird. Das Volumen dieses Polyëders kann in folgender Form geschrieben werden :

$$V = q(n_1^3 + n_2^3 + n_3^3 + \dots),$$

wobei q eine Constante ist.

“Da das Polyëder ein Minimum der Oberflächenenergie bei constanten Volumen besitzen muss, so müssen folgende Bedingungen erfüllt werden :

$$dE = 2p(k_1 n_1 dn_1 + k_2 n_2 dn_2 + k_3 n_3 dn_3 \dots) = 0;$$

$$dV = 3q(n_1^2 dn_1 + n_2^2 dn_2 + n_3^2 dn_3 + \dots) = 0,$$

dieses ist aber nur dann möglich, wenn

$$k_1 : k_2 : k_3 \dots = n_1 : n_2 : n_3 : \dots$$

This proof, however, is faulty; for in writing down the expressions for E and V —which should be $(k_1 p_1 n_1^2 + k_2 p_2 n_2^2 + \dots)$ and $\frac{1}{3}(p_1 n_1^3 + p_2 n_2^3 + \dots)$ respectively, where $p_1, p_2, \dots$ are constants: this, however, does not affect his argument,—he has assumed the ratios $n_1 : n_2 : n_3 \dots$ constant, and therefore in the expressions for dE and dV , $dn_1 : dn_2 : dn_3 \dots$ will be constant; but in deducing $k_1 : k_2 : k_3 \dots = n_1 : n_2 : n_3 \dots$, from $dE = dV = 0$ he tacitly assumes $dn_1, dn_2, dn_3 \dots$ quite independent. His result, however, is correct, as the following proof shows:—

Suppose $s_1, s_2, s_3 \dots$ the areas of the faces $\sigma_1, \sigma_2, \sigma_3 \dots$ perpendicular to the normals through any point whose lengths are $n_1, n_2, n_3 \dots$ respectively. We have then

$$V = \frac{1}{3} \sum ns \quad \text{and} \quad \therefore dV = \frac{1}{3} \sum (nds + sdn).$$

Now if a polyhedron undergoes a small deformation, the normals to its faces remaining fixed in direction, we have $dV = \sum sdn$; for suppose the polyhedron to be immersed in a weightless incompressible fluid which is contained in a cylinder of cross-section A , closed at the top with a movable piston of weight W . Then the pressure at any point of the liquid is $\frac{W}{A}$.

If now the polyhedron undergoes a small deformation of the kind stated above, the work done by any surface lies between

$$\frac{W}{A} (s + ds) dn \quad \text{and} \quad \frac{W}{A} s dn, \quad \text{and} \quad \therefore = \frac{W}{A} s dn,$$

neglecting small quantities of the second order. If now the polyhedron's volume increases by a quantity dV , the piston is

forced through a height $\frac{dV}{A}$; and therefore the work done by the surfaces of the polyhedron is $W \frac{dV}{A}$;

$$\text{and } \therefore W \frac{dV}{A} = \Sigma \frac{W}{A} s dn, \text{ and } \therefore dV = \Sigma s dn.$$

Hence

$$dV = \frac{1}{3} \{ \Sigma (nds) + dV \} \text{ and } \therefore \Sigma nds = 2dV.$$

Now we have relations between $s_1, s_2, s_3 \dots$ due to the fact that they can form polyhedron faces whose normals have fixed directions. For take any point of reference O, and take planes $P_1, P_2, P_3 \dots$ through O, parallel to $\sigma_1, \sigma_2, \sigma_3 \dots$.

Consider any point A; let the perpendiculars from O on the surfaces of the polyhedron be $n_1, n_2, n_3 \dots$, and from A be $n_1^a, n_2^a, n_3^a \dots$; and let the perpendiculars from A on $P_1, P_2, P_3 \dots$ be $a_1, a_2, a_3, a_4, a_5, \dots$ (considered positive or negative, as A and the corresponding polyhedron surface are on the same or different sides of the corresponding plane P). Then $\Sigma ns = \Sigma n^a s$; for each $= 3V$; and

$$\therefore \Sigma (n - n^a) s = 0, \text{ and } \therefore \Sigma as = 0, \text{ (for } n_1 - n_1^a = a_1, \text{ \&c.)}$$

Now $a_1, a_2, a_3 \dots$ are sufficient to completely fix the position of the point A with reference to O, and there are linear relations of the type

$$a_4 = p_4 a_1 + q_4 a_2 + r_4 a_3; \quad a_5 = p_5 a_1 + q_5 a_2 + r_5 a_3; \quad \&c.$$

Take other points B, C, D, $\dots$, and let $b, c, d, \dots$ correspond to a . Then we have $\Sigma as = 0, \Sigma bs = 0, \Sigma cs = 0, \Sigma ds = 0, \dots$; an indefinite number of relations, but only equivalent to 3 *independent* relations; for choosing λ, μ, ν so that

$$\lambda a_1 + \mu b_1 + \nu c_1 = d_1; \quad \lambda a_2 + \mu b_2 + \nu c_2 = d_2; \quad \lambda a_3 + \mu b_3 + \nu c_3 = d_3;$$

we have

$$\begin{aligned} d_4 &= p_4 d_1 + q_4 d_2 + r_4 d_3 = p_4 (\lambda a_1 + \mu b_1 + \nu c_1) + q_4 (\lambda a_2 + \mu b_2 + \nu c_2) \\ &\quad + r_4 (\lambda a_3 + \mu b_3 + \nu c_3) = \lambda (p_4 a_1 + q_4 a_2 + r_4 a_3) + \mu (p_4 b_1 + q_4 b_2 + r_4 b_3) \\ &\quad + \nu (p_4 c_1 + q_4 c_2 + r_4 c_3) = \lambda a_4 + \mu b_4 + \nu c_4; \end{aligned}$$

and similarly

$$d_5 = \lambda a_5 + \mu b_5 + \nu c_5, \quad \&c.;$$

and hence

$$\Sigma ds = \lambda \Sigma as + \mu \Sigma bs + \nu \Sigma cs.$$

We have then

$$\Sigma nds = 2dV; \quad \Sigma kds = dE; \quad \text{and } \Sigma ads = \Sigma bds = \Sigma cds = 0;$$

and for V constant and E a minimum we have

$$0 = \Sigma nds = \Sigma kds = \Sigma ads = \Sigma bds = \Sigma cds;$$

where the quantities ds are connected *only* by these five equations.

Hence we have

$$\begin{aligned} n_1 - \alpha a_1 - \beta b_1 - \gamma c_1 - \rho k_1 &= 0, \\ n_2 - \alpha a_2 - \beta b_2 - \gamma c_2 - \rho k_2 &= 0, \\ n_3 - \alpha a_3 - \beta b_3 - \gamma c_3 - \rho k_3 &= 0, \\ \&c. \qquad \qquad \&c. \end{aligned}$$

where $\alpha, \beta, \gamma, \rho$ are (unknown) constants.

Now there can always be found a point O_1 , whose distances from P_1, P_2, P_3 are

$$\alpha a_1 + \beta b_1 + \gamma c_1, \quad \alpha a_2 + \beta b_2 + \gamma c_2, \quad \alpha a_3 + \beta b_3 + \gamma c_3$$

respectively; the distance of O_1 from P_4 is

$$\begin{aligned} p_4(\alpha a_1 + \beta b_1 + \gamma c_1) + q_4(\alpha a_2 + \beta b_2 + \gamma c_2) + r_4(\alpha a_3 + \beta b_3 + \gamma c_3) \\ = \alpha(p_4 a_1 + q_4 a_2 + r_4 a_3) + \beta(p_4 b_1 + q_4 b_2 + r_4 b_3) \\ + \gamma(p_4 c_1 + q_4 c_2 + r_4 c_3) = \alpha a_4 + \beta b_4 + \gamma c_4. \end{aligned}$$

Similarly its distance from P_5 is $\alpha a_5 + \beta b_5 + \gamma c_5$, &c.

Hence if the perpendiculars from O_1 on $\sigma_1, \sigma_2, \sigma_3, \dots$ are $n'_1, n'_2, n'_3, \dots$, we have

$$\begin{aligned} n'_1 = n_1 - \alpha a_1 - \beta b_1 - \gamma c_1 = \rho k_1, \quad n'_2 = n_2 - \alpha a_2 - \beta b_2 - \gamma c_2 = \rho k_2, \\ n'_3 = n_3 - \alpha a_3 - \beta b_3 - \gamma c_3 = \rho k_3, \quad \&c. \quad \&c. \end{aligned}$$

Hence there is a point O_1 for which

$$n'_1 : n'_2 : n'_3 : \dots = k_1 : k_2 : k_3 : \dots,$$

which is Wulff's theorem.

It is not always easy to apply the above theorem to the case of an actual crystal. It seems therefore worth while to give an example which is of use in many cases.

Let three planes OBC, OCA, OAB meet along the lines OA, OB, OC ; and let them be met by two planes $ABC, A'B'C'$, so that $OA = xa, OB = xb, OC = xc$; $OA' = ya', OB' = yb', OC' = yc'$, where a, b, c, a', b', c' are supposed known. Let the angles BOC, COA, AOB be α, β, γ , respectively.

Then the volume of the figure $OABC$ is

$$\frac{x^3 abc}{6} \sqrt{1 + 2 \cos \alpha \cdot \cos \beta \cdot \cos \gamma - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma},$$

and of $OA'B'C'$ is

$$\frac{y^3 a' b' c'}{6} \sqrt{1 + 2 \cos \alpha \cdot \cos \beta \cdot \cos \gamma - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma};$$

the area of ABC is

$$\frac{x^2}{2} \sqrt{\Sigma (b^2 c^2 \sin^2 \alpha - bc(b^2 + c^2) \cos \alpha + 2a^2 bc \cos \beta \cdot \cos \gamma)};$$

the area of OBC is $\frac{x^2}{2} bc \sin \alpha$, and of OB'C' is $\frac{y^2 b' c'}{2} \sin \alpha$;

and we get the areas of A'B'C', OCA, OC'A', OAB, OA'B' similarly.

Suppose now that the figure ABCA'B'C' represents a crystal which is such that its surface energy is a minimum for a given volume. Let the capillarity constants of the faces BC'B'C', CAC'A', ABA'B', ABC, A'B'C' be k_1, k_2, k_3, k , and k' , respectively; then the volume of the crystal is

$$\frac{1}{6} \sqrt{(1 + 2 \cos \alpha \cdot \cos \beta \cdot \cos \gamma - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma)} (x^3 abc - y^3 a' b' c'),$$

and the surface energy is $P_1 x^2 - P_2 y^2$, where

$$P_1 = \frac{1}{2} (bc k_1 \sin \alpha + ca k_2 \sin \beta + ab k_3 \sin \gamma + k \sqrt{\Sigma (b^2 c^2 \sin^2 \alpha - bc(b^2 + c^2) \cos \alpha + 2a^2 bc \cos \beta \cdot \cos \gamma)}),$$

$$P_2 = \frac{1}{2} (b' c' k_1 \sin \alpha + c' a' k_2 \sin \beta + a' b' k_3 \sin \gamma - k' \sqrt{\Sigma (b'^2 c'^2 \sin^2 \alpha - b' c' (b'^2 + c'^2) \cos \alpha + 2a'^2 b' c' \cos \beta \cdot \cos \gamma)}).$$

We have then at once for constant volume and surface energy a minimum, on differentiating

$$\frac{x}{y} = \frac{P_1 a' b' c'}{P_2 abc}; \text{ with the condition } \frac{P_1^4 a'^2 b'^2 c'^2}{P_2^3 a^2 b^2 c^2} - P_1 > 0.$$

Magdalen College, Oxford.